

Symmetry-Based Tight Binding Modeling of Halide Perovskite Semiconductors

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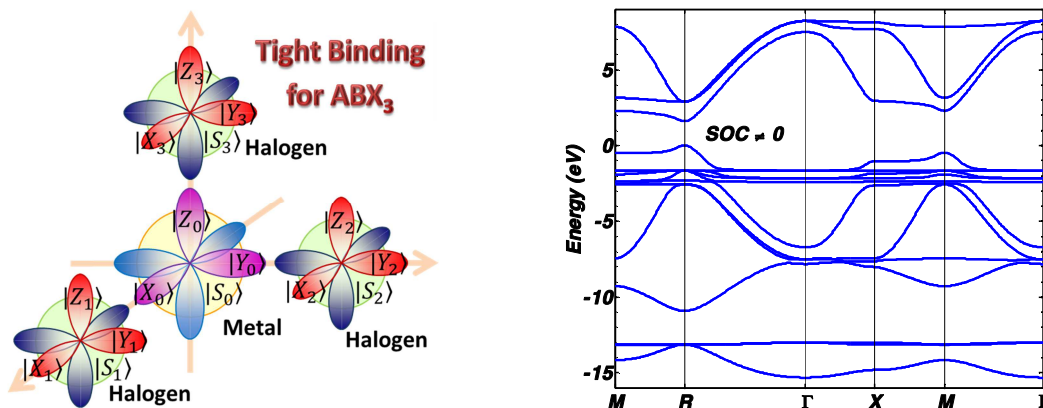
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Empirical and semi-empirical models are particularly suited to address issues related to complex structures. Based on a general symmetry analysis, herein we build an empirical sp^3 tight-binding (TB) model for the reference $Pm\bar{3}m$ cubic phase of halide perovskite structures of general formula ABX_3 . This TB model includes 16 and 32 basis functions without and with spin orbit coupling (SOC), respectively¹. The 16 basis functions are made of one “s” and three “p” orbitals for the metal atom B, and the same for three halide atoms X atoms. No basis function is taken into account for the A organic molecule, which position cannot be fixed in the cubic phase. The TB electronic band diagram, with and without SOC of MAPbI₃, is determined based on state of the art density functional theory results that include many body correction (DFT+GW)². The band gap is obtained at the R -point with $E_G = 1.603$ eV. Close to the band gap, effective masses are: $m_h^* = 0.215 m_0$ for the valence band and $m_e^* = 0.218 m_0$ for the conduction band, which leads to a reduced effective mass of $0.108 m_0$, all data being consistent with experimental values.^{3,4}

This TB model affords an atomic-scale description to computing various properties, including distorted structures, at a significantly reduced computational cost. The powerfulness of the present TB Hamiltonian is exemplified with the calculation of band-to-band absorption spectra, the variation of the band gap under volumetric strain, as well as the Rashba effect⁵ for a uniaxial symmetry breaking. Compared to first-principles approaches, such a semi-empirical model permits us to tackle more difficult issues in terms of size with complex heterostructures, nanostructures or composite materials as well as diversity of physical phenomenon under investigation. It should be as relevant to the future of perovskite device modeling, as it has proved efficient for conventional semiconductors.



Figures: Schematic representation of the tight-binding atomic orbitals and MAPbI₃ band diagram obtained within the TB scheme with SOC.

Références :

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